

# Levels of Toxic Metals in Marine Organisms Collected from Southern California Coastal Waters

by Bruce A. Fowler,\* Rimmon C. Fay,† Richard L. Walter,‡ Robert D. Willis,‡ and William F. Gutknecht\*\*

Emission of toxic trace metals into southern California coastal waters has resulted in the extensive accumulation of the elements within marine sediments. The current study was undertaken to evaluate concentrations of trace metals in bottom-dwelling marine fauna collected from two sampling areas. Analyses carried out on muscle samples of the dover sole (*Microstomus pacificus*) and the crab (*Cancer anthonyi*) by proton-induced x-ray emission analysis showed considerable concentrations of arsenic and selenium. Samples of gonads, digestive gland, and muscle from the crab *Mursia gaudichaudii* analyzed by atomic absorption spectroscopy showed elemental concentrations in muscle similar to the crab *Cancer anthonyi* and much higher metal levels in gonad and digestive gland. These findings suggest the need for further studies concerning the relationship between emission of metals into the marine environment and their abundance in marine fauna.

Many tons of trace metals, potentially toxic to marine life, are annually released into the southern California coastal basins as a result of industrialization and urbanization in the Los Angeles area (1). These elements have accumulated to high concentrations in the bottom sediments of these basins (1-4). Tissue burdens of trace metals in organs of bottom dwelling marine species inhabiting the basins have received only limited attention (5). This report details levels of 18 trace elements in muscle samples of the dover

sole (*Microstomus pacificus*) and crab (*Cancer anthonyi*) as determined by proton-induced x-ray emission analysis (PIXEA) and concentrations of zinc, copper, lead, cadmium, mercury, arsenic, and chromium found in samples of digestive gland (hepato-pancreas), gonad, and muscle from specimens of the crab *Mursia gaudichaudii* by atomic absorption spectroscopy.

These analytical studies were undertaken because oceans and coastal waters act as sinks for trace elements emitted into the environment and it is known that marine organisms consumed as food by man may accumulate trace elements to high levels. Knowledge concerning the levels of toxic metals within this valuable food source is essential to performing meaningful toxicological evaluation studies, since metals bound to tissues of marine organisms may be more or less toxic due to metal-metal interactions and altered absorption, distribution, and excretion characteristics.

\*Environmental Toxicology Branch, National Institute of Environmental Health Sciences, Research Triangle Park, N.C. 27709.

†Pacific Bio-Marine Supply Company, P.O. Box 536, Venice, Calif. 90291.

‡Department of Physics, Duke University, Durham, N.C. 27709.

\*\*Department of Chemistry, Duke University, Durham, N.C. 27709.

## Materials and Methods

Eleven dover sole, 15–20 cm in length and 14 crabs (*Cancer*) with carapace widths of 15–20 cm were collected by trawling in 55–69 fathoms of water near Point Vicente, Palos Verdes. This area was designated the “contaminated region” due to the high known concentrations and accumulation rates of toxic metals in the bottom sediments (2, 4). Twelve dover sole and 14 crabs (*Cancer*) of comparable size were also collected at similar depths off Santa Barbara. This area was considered the “noncontaminated region,” since metal accumulation rates and concentrations in sediments of this area have not changed greatly in the past century (4). Lead concentrations in the sediments from the noncontaminated area, for example, are some 12–60 times less than those found off Point Vicente.

Muscle samples from the animals were frozen in plastic bags and freeze-dried in a vacuum prior to mounting on Formvar target rings for proton-induced x-ray emission analysis (PIXEA). The freeze-drying process did not alter muscle mercury

concentrations when tested against frozen sections. The beam generation, x-ray detection limits, and counting procedures utilized for this study have been extensively described elsewhere (6).

In addition to PIXEA studies, tissue samples of muscle, hepato-pancreas and gonad from 10 male *Mursia* with carapace widths of 9.0–12 cm were also collected in the contaminated region and frozen in plastic bags prior to digestion in nitric and sulfuric acids. Diluted samples were analyzed for the above elements by using a Perkin-Elmer Model 303 atomic absorption spectrophotometer. The detection limits in parts per million (ppm) or parts per billion (ppb) of wet weight for each of the elements studied were as follows: zinc, 0.625 ppm; copper, 1.25 ppm; chromium, 0.75 ppm; lead, 0.625 ppm; cadmium, 0.0625 ppm; mercury, 2.5 ppb; arsenic, 1.25 ppm.

## Results

PIXEA evaluation of fish and crab muscle tissue indicated that many trace elements were present, although it was not possible to determine

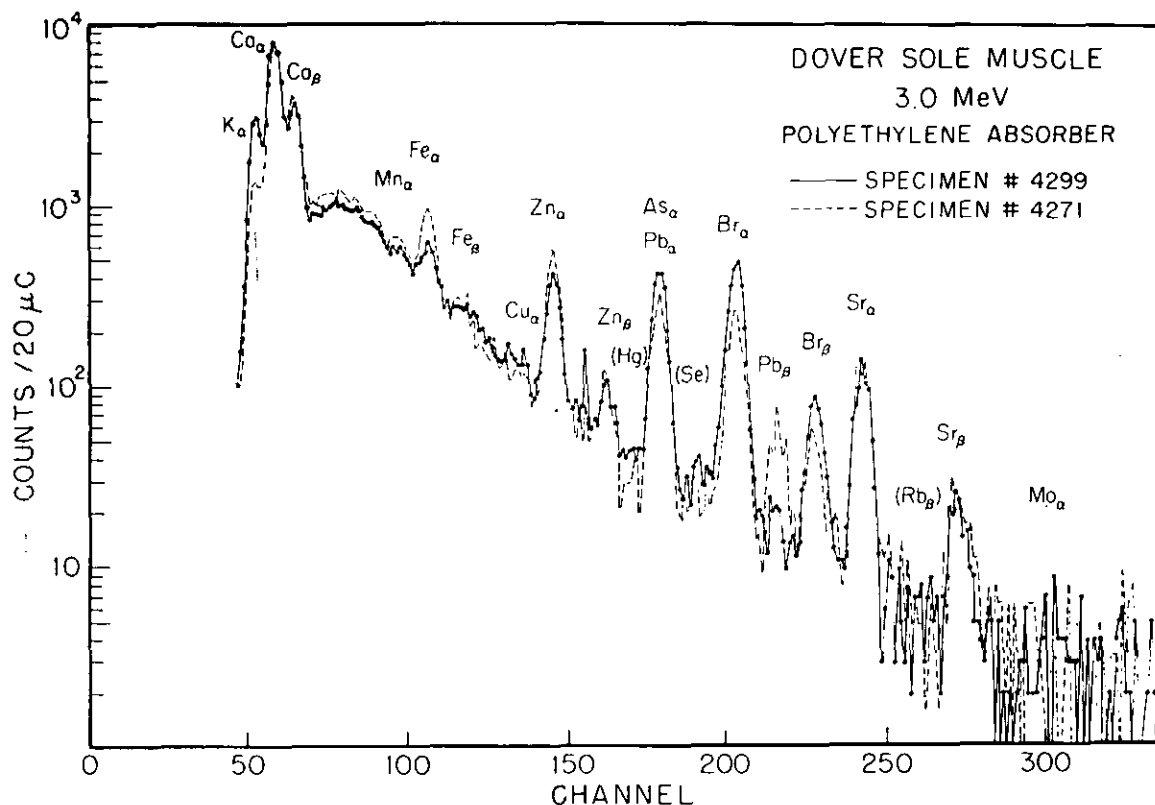


FIGURE 1. PIXEA spectra from two dover sole superimposed upon each other. Note prominent zinc, arsenic, lead, bromine, and strontium peaks.

whether the values obtained had any relation to high bottom sediment levels for many of the metals.

Typical PIXEA spectra from muscle samples of two dover sole are presented in Figure 1. Arsenic, lead, and selenium are the primary toxic elements of interest. Graphs showing mean levels and high and low ranges for individual elements within muscle samples of dover sole collected from the contaminated and noncontaminated areas are presented in Figures 2 and 3, respectively.

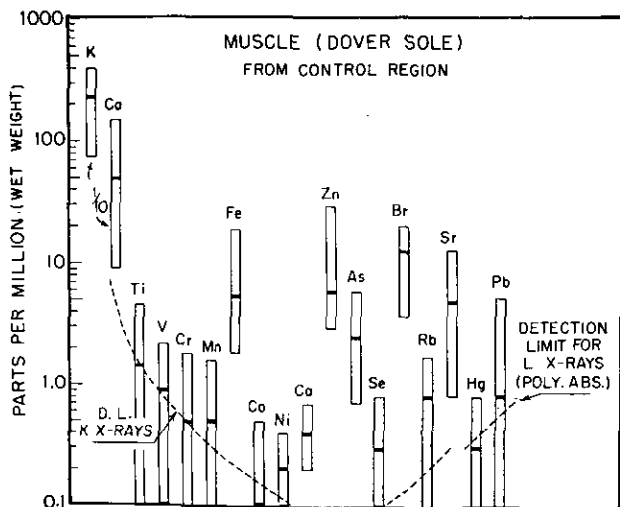


FIGURE 2. Summary of PIXEA data for muscle of dover sole collected in the non-contaminated area. Highest and lowest elemental values are indicated by ends of each bar. Means are indicated by horizontal black lines. The dotted line represents a  $3\sigma$  detection limit which is a function of the peak to background ratio for x-rays of a given element (6).

Muscle samples from the dover sole examined by PIXEA had high levels of potassium and calcium. Bromine, zinc, iron, arsenic, and strontium were next in order of abundance. Lead, vanadium, titanium, manganese, chromium, cobalt, nickel, copper, selenium, rubidium, and mercury were present in concentrations of 1 ppm or less. No differences in muscle concentrations of these elements were observed between the two areas sampled except for arsenic which was approximately 2-fold higher in fish collected from the contaminated area ( $p < 0.05$ ).

PIXEA evaluation of muscle samples from the crabs (*Cancer anthonyi*) showed a similar pattern of relative metal abundance although many elements are present at concentrations higher than those of dover sole (Figs. 4 and 5). Arsenic and selenium, in particular, were present in higher concentrations within these samples than in those of

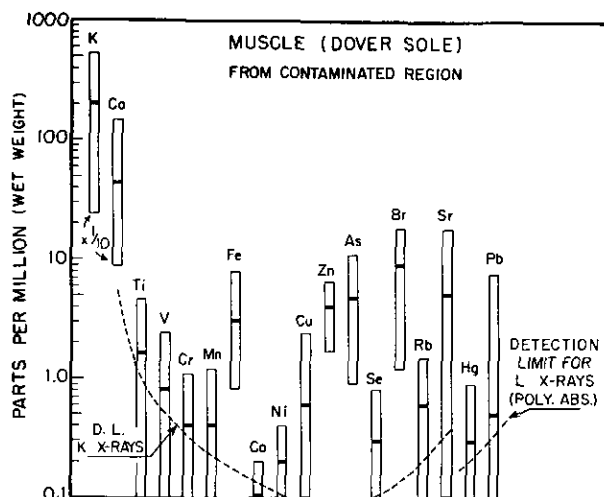


FIGURE 3. Summary of PIXEA values obtained from muscle samples of dover sole collected in the contaminated area. Note higher mean arsenic values in comparison with dover sole collected from the noncontaminated area. This difference was significant at  $p < 0.05$  using a Mann-Whitney U test.

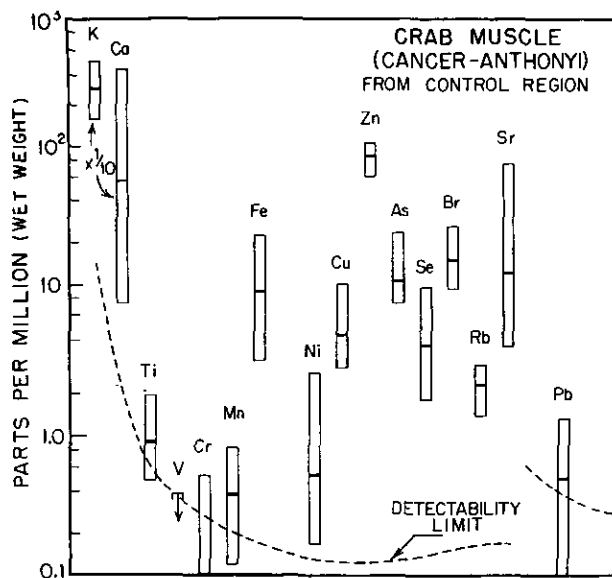


FIGURE 4. Summary of PIXEA data obtained for muscle samples of the crab (*Cancer anthonyi*) collected in the noncontaminated area showing mean, high, and low values. Note higher concentrations of arsenic and selenium than in muscle of dover sole.

the dover sole. In contrast to the dover sole, mean arsenic and selenium values were higher in crabs collected from the noncontaminated region than in those collected from the contaminated area ( $p < 0.01$ ). The results of statistical analyses for arsenic and selenium concentrations in muscle samples

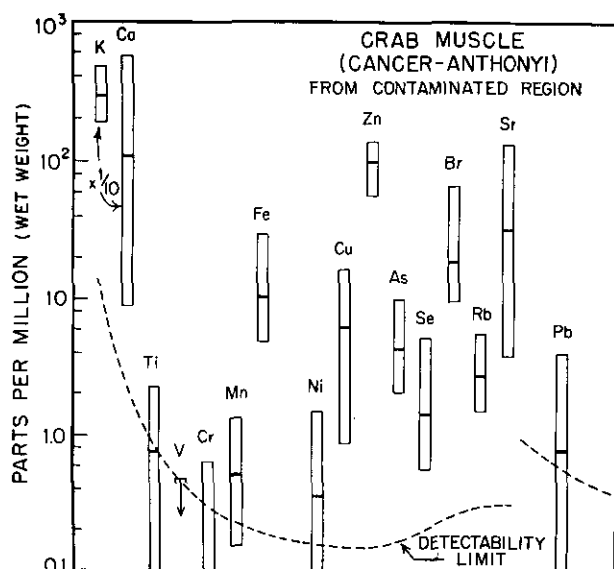


FIGURE 5. Summary of values obtained by PIXEA from muscle samples of *Cancer anthonyi* collected in the contaminated area showing mean, high and low values. Mean arsenic and selenium values were lower ( $p < 0.01$ , Mann-Whitney U test) for this group than those collected in the noncontaminated area.

from dover sole and *Cancer anthonyi* are presented in Table 1.

Data from atomic absorption analyses of different organs in the crab *Mursia* are presented in Table 2 and show muscle elemental concentrations similar to those found in the *Cancer anthonyi* examined by PIXEA.

From these data, it is clear that most organs of the *Mursia* studied had considerable levels of these

Table 1. Concentrations of arsenic and selenium in muscle samples of Dover sole (*Microstomus pacificus*) and crabs (*Cancer anthonyi*) collected in contaminated and noncontaminated areas.

Sample and source	Arsenic, ppm <sup>a</sup>	Selenium, ppm <sup>a</sup>
<i>Microstomus pacificus</i>		
Noncontaminated area	2.43 ± 0.37	0.38 ± 0.06
Contaminated area	4.12 ± 0.62 <sup>b</sup>	0.27 ± 0.05
<i>Cancer anthonyi</i>		
Noncontaminated area	51.02 ± 5.12	15.66 ± 2.75
Contaminated area	17.29 ± 1.80 <sup>c</sup>	5.14 ± 0.96 <sup>c</sup>

<sup>a</sup>Mean ± SEM, on wet weight basis.

<sup>b</sup> $p < 0.05$  (two-sided Mann-Whitney U Test).

<sup>c</sup> $p < 0.01$  (two-sided Mann-Whitney U Test).

elements with the exception of chromium which was not detected in any of the samples analyzed. In general, the digestive glands and gonads had much higher levels of elements than did muscle samples. Considerable inter-animal variation was observed in tissue levels of the metals and not all samples had every element. Zinc, copper, mercury, and arsenic were found in most of the samples while lead and cadmium showed wider distributional variability. Analysis of selected samples by gas-liquid chromatography for mercury disclosed that all of the mercury present was in the form of methyl mercury. Considerable arsenic concentrations approximating those of *Cancer anthonyi* were consistently found within all of the analyzed specimens. This element was more abundant in the digestive gland and gonad than in muscle.

Table 2. Trace metal concentrations from tissue samples of *Mursia gaudichaudii* collected in the Santa Monica Basin<sup>a</sup>.

	Zn	Cu	Pb	Cd	Hg (total)	As	Cr <sup>b</sup>
Digestive gland							
N <sup>c</sup>	10	10	5	10	8	10	
Mean level, ppm	70.10	88.67	4.28	14.62	0.2725	12.24	
SEM, ppm	7.28	24.0	2.15	4.80	0.0648	2.44	
Range, ppm	21.4-97.1	13.9-194.5	1.2-12.6	0.2-38.4	0.08-0.62	3.27-25.80	
Gonad							
N <sup>c</sup>	10	10	4	10	8	10	
Mean level, ppm	22.11	23.46	18.57	5.89	0.321	9.19	
SEM, ppm	3.53	5.64	16.08	2.17	0.189	3.14	
Range, ppm	9.2-42.5	4.28-54.7	0.86-66.8	0.2-18.1	0.013-0.137	3.79-30.54	
Muscle							
N <sup>c</sup>	10	10	7	2	8	10	
Mean level, ppm	42.90	15.77	5.20	0.80	0.3275	6.23	
SEM, ppm	2.74	0.975	1.64	0.19	0.0605	0.97	
Range, ppm	27.8-54.8	12.3-20.8	1.6-13.3	0.6-1.0	0.11-0.58	2.10-10.08	

<sup>a</sup>In ppm of wet weight.

<sup>b</sup>Chromium was not detected in any of the samples analyzed.

<sup>c</sup>N equals the number of samples out of 10 which contained detectable amounts of a specific metal. Mean levels and standard errors are calculated on the basis of N.

## Discussion

The current study indicates that many trace elements are present in some bottom dwelling marine animals at concentrations higher than those commonly measured in canned food stuffs. Arsenic was the most prevalent element considered toxic to humans. This finding supports studies by Le Blanc and Jackson (7) and Peden et al., (8) that marine organisms accumulate arsenic from their environment. More work is needed on the chemical form of arsenic in these tissues and the mechanisms by which it is accumulated since the toxicity of arsenicals is known to vary greatly with oxidation state and chemical form. Differences in the chemical form of the arsenic found in muscle of dover sole and crabs could explain why dover sole have lower concentrations than crabs. A similar phenomenon could explain why dover sole in the contaminated area had higher arsenic concentrations than in the noncontaminated area while the reverse was true for crabs.

The wide individual variation in concentrations of cadmium, copper, zinc, lead, and other elements observed in this study is similar to that reported by Topping (9) in viscera of crabs (*Cancer pagurus*) and lobsters (*Homarus vulgaris*) taken from Scottish waters. Factors which influence these differences are currently undefined. In the current study, excessive fouling of the nets by sludge in the contaminated region of the sea bottom (10) necessitated collection of the specimens at the periphery of this area. Considering the migratory habits of both dover sole and crabs, wide variation in individual burdens may not be unexpected due to movement in and out of this area. It is also possible that death occurs among those individuals whose total body burden of trace metal exceeds some limit and that they will be replaced by others migrating from a less contaminated area. Advective transport (1) of metals of by the California current may also complicate local assessment of altering metal concentrations in the water column of both contaminated and noncontaminated areas.

The above findings are also of interest because they indicate that muscle and viscera of bottom dwelling marine organisms living in an environment greatly enriched with trace metals do have considerable burdens of these elements although it is currently not possible to conclude that these levels are a reflection of metal concentration in bottom sediments. Previous reports by others on trace metal uptake by marine organisms have concentrated on more pelagic species such as the tuna

and swordfish, which occupy a greatly different ecological niche from benthic scavengers such as crabs. More extensive studies on bottom-dwelling marine fauna for metal concentrations and toxicity seem in order.

Another point of note is that enrichment of coastal waters and the ocean floor by toxic trace metals has been occurring near other large seaport cities such as New York (11) and Baltimore (12). The effects of toxic trace metals on marine fauna living in contaminated areas of sea bottom is thus a general problem which is not limited southern California. Trace element emission into coastal waters also needs to be examined for its impact on the ability of marine organisms to survive and reproduce. Evaluation of important and valuable coastal fisheries is necessary prior to the future development of industries or power plants near the marine environment.

Finally, the above data suggest the need for epidemiological evaluation of human populations consuming large quantities of fish and shellfish for signs of trace metal toxicity. Experimental animal studies are needed to compare the absorption, distribution, excretion, and toxicity of metals bound to fish or shellfish tissue with the same metals administered by inhalation or consumption of contaminated drinking water. A realistic assessment of trace metals as toxicants in man's environment is essential to establishing meaningful pollution guidelines.

## REFERENCES

1. Young, D.R., Young, C.S., and Hlavka, G. E. Sources of trace metals from highly-urbanized Southern California to the adjacent marine ecosystem. In: *Cycling and control of metals: Proceedings of an Environmental Resources Conference*, U.S. Environmental Protection Agency, National Environment Research Center, Cincinnati, Ohio 1973, pp. 21-39.
2. Galloway, J. N. Man's alteration of the natural geochemical cycle of selected trace elements. Doctoral Thesis, University of California, San Diego, 1972, 143 pp.
3. Chow, T. J., et al. Lead pollution: records in southern California coastal sediments. *Science* 181: 551 (1973).
4. Bruland, K. W., et al. History of metal pollution in southern California coastal zone. *Environ. Sci. Technol.* 8: 425 (1974).
5. Klein, D. H., and Goldberg, E. D. Mercury in the marine environment. *Environ. Sci. Technol.* 4: 765 (1970).
6. Walters, R. L., et al. Analysis of biological, clinical, and environmental samples using proton-induced X-ray emission. *Anal. Chem.* 46: 843 (1974).
7. Le Blanc, P. J., and Jackson, A. L. Arsenic in marine fish and invertebrates. *Marine Pollut. Bull.* 4: 88 (1973).

8. Peden, J.D., et al. Heavy metals in Somerset marine organisms. *Marine Pollut. Bull.* 4: 7 (1973).
9. Topping, G. Heavy metals in shellfish from scottish waters. *Aquaculture*. 1: 379 (1973).
10. Parkhurst, J. D. Technical report on waste discharge to the ocean. Sanitation Districts of Los Angeles County, 1: 111 (1973).
11. Carmody, D. J. Pearce, J. B., and Yasso, W. E. Trace metals in sediments of the New York Bight. *Marine Pollut. Bull.* 4: 132 (1973).
12. Palmer, H.D. Trace metals investigations. In: *Chester River Study*. W.D. Clarke and H.D. Palmer, Eds., State of Maryland Department of Natural Resources and Westinghouse Electric Corporation, Vol. 2, 1972, p. 47.